

NO emissions in oxy-coal combustion with the addition of steam in an entrained flow reactor

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ABSTRACT

The NO emissions of a semi-anthracite and a high-volatile bituminous coal were studied under oxy-fuel combustion conditions in an entrained flow reactor (EFR). The results obtained under oxy-fuel atmospheres (21%O₂-79%CO₂, 30%O₂-70% O₂ and 35%O₂-65%CO₂), were compared with those produced in air. The replacement of CO₂ by 5, 10 and 20% of steam in the oxy-fuel combustion atmospheres was also evaluated in order to study the wet recirculation of flue gas. The NO emissions during oxy-fuel combustion were lower than those in air-firing, and a slight increasing trend in NO emissions was observed as O₂ concentrations in the oxy-fuel atmospheres increased. Similarly, the NO concentration was reduced by the addition of steam, both under air and under oxy-fuel atmospheres, but no relevant differences between the different steam concentrations were observed.

Keywords: Entrained flow reactor; NO emissions; Oxy-fuel combustion; Pulverized coal; Steam addition

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1 INTRODUCTION

The combustion of fossil fuels results in the formation of nitrogen oxides (NO_x), either via the fixation of atmospheric nitrogen (thermal or prompt mechanisms), or by the conversion of nitrogen-containing structures in the fuel (fuel-bound nitrogen oxidation). Coal is a cheaper and more abundant resource than other fossil fuels, such as oil and natural gas, while at the same time being a reliable fuel for power production.¹ Coal is part of the greenhouse problem, since the main emissions from coal combustion are sulphur dioxide, nitrogen oxides, particulates and carbon dioxide.² For a long time, the mechanisms behind the formation and destruction of NO_x have been the subject of extensive investigations.³

In recent years, the oxy-fuel combustion process, which consists of the burning of fuel in a mixture of oxygen and recycled flue gases (mainly CO_2 and H_2O), has come to be regarded as a very promising technology for capturing CO_2 from fossil fuel power plants. The exhaust flue gas consists of approximately 95% of CO_2 on a dry basis, the remaining part being mainly excess oxygen from combustion, nitrogen and, to lesser extent, pollutants, such as nitrogen oxides (NO_x) and sulphur oxides (SO_x) (approximately 0.1-0.2%). Control of these contaminants is required for emissions into the environment, since NO_x causes acid rain and formation of ground level ozone, and potentially for CO_2 storage.⁴ In oxy-firing, nitrogen is excluded from the combustion and the volume of flue-gas is reduced by around 80% compared to air-firing. Furthermore, most of the flue gas is extracted for storage and only around 10% of the gas generated is emitted to the atmosphere.⁴

It has been shown that a significant reduction of NO_x can be achieved with oxy-fuel combustion in relation to air-firing.^{5,6} This substantial NO_x reduction is partly due to the

suppression of thermal NO formation due to firstly the absence of atmospheric N₂ and, secondly, because recycled NO is reduced to molecular nitrogen after being introduced into the flame zone. Nitrogen oxides include nitric oxide (NO) and nitrogen dioxide (NO₂). NO is the most important nitrogen-oxygen product of combustion, but it could be further oxidized to NO₂ at low temperatures.

A number of previous works have already dealt with NO emissions under oxy-fuel combustion conditions,⁶⁻⁹ in which it is shown that lower emissions can be achieved with oxy-fuel combustion than with air-firing. However, the use of steam in the oxidizer stream has only occasionally been mentioned.^{10,11} Recently, Smart et al.¹² pointed out that the combustion of coal in an O₂/CO₂/H₂O atmosphere (including ignition, burnout, flame stability and emissions) was a topic worthy of study.

In the present work, an entrained flow reactor (EFR) was used in order to study the effect of replacing N₂ with CO₂ in a combustion atmosphere, and the effect of enhanced levels of O₂ in an oxy-fuel combustion atmosphere upon NO emissions from coal combustion. The addition of steam was evaluated in order to study the effect of the wet recirculation of flue gas.

2 EXPERIMENTAL

2.1 Coals

Two coals of different rank were used in this work: a semi-anthracite (HVN) and a high-volatile bituminous coal (BA). The samples were ground and sieved to obtain a particle size fraction of 75-150 µm. The results of the proximate and ultimate analyses and the high heating values of the samples are presented in Table 1.

2.2 Experimental facility and operation procedures

An entrained flow reactor was used to study the NO emissions in oxy-coal combustion at high heating rates and short residence times. A diagram of the experimental device used is shown in Fig. 1. The reactor has a reaction zone with a maximum length of 1.7 m and an internal diameter of 0.04 m. The EFR is electrically heated and is able to work at a maximum temperature of 1100 °C. Coal samples were fed from a hopper and the mass flow was controlled using a mechanical feeding system. The samples were introduced through an air-cooled injector to ensure that the temperature did not exceed 100 °C before entering the reaction zone. The gases were preheated to the oven temperature before being introduced into the reactor through flow straighteners. The flow rates of N₂, CO₂ and O₂ from the gas cylinders were controlled by mass flow controllers. The steam was generated by a vaporizer, in which water was heated up to 250 °C. A HPLC pump was used to control the flow rate of water towards the vaporizer. The steam was then mixed with the inlet gases before they were introduced into the pre-heater. A water-cooled collecting probe was inserted into the reaction chamber from below. Nitrogen was introduced at the top of this probe to quench the reaction products. Particles were removed by means of a cyclone and a filter, and the exhaust gases were monitored using a battery of analysers (O₂, CO₂, CO, NO and SO₂). The experimental errors in the measurements was around 5%. During the combustion experiments, the reactor was kept at a temperature of 1000°C and a particle residence time of 2.5 s was employed.

Four binary mixtures of O₂, N₂ and CO₂ and several ternary mixtures of O₂, N₂, CO₂ and H₂O(v) were used to study the behaviour of the coals. Thus, air (21%O₂-79%N₂) was used as reference and three binary mixtures of O₂ and CO₂ were compared (21%O₂-

79%CO₂, 30%O₂-70% O₂ and 35%O₂-65%CO₂). Moreover, the addition of 5, 10 and 20% of steam to the air and the oxy-fuel combustion atmospheres, as a replacement for N₂ or CO₂, respectively, was evaluated in order to study the effect of the wet recirculation of flue gas on NO emissions from the oxy-fuel combustion of coal.

3 RESULTS AND DISCUSSION

Coals HVN and BA were burned under different levels of excess oxygen for each atmosphere studied. The fuel ratio, defined as the ratio between the coal mass flow rate and the stoichiometric value, was used to assess the excess oxygen during combustion. The NO concentrations (mg NO/mg burned coal) of coals HVN and BA under the different atmospheres employed, both with and without the addition of steam, are shown in Fig. 2 and 3, respectively. A decrease in NO concentration was observed as the fuel ratio increased, since the lesser amount of oxygen available at higher fuel ratios would reduce coal burnout.

For a better comparison, the behaviour of coals under air and oxy-fuel atmospheres, NO concentrations were interpolated at a fuel ratio of 0.8 using the graphs shown in Fig. 2 and 3. The results for both coals, HVN and BA, are presented in Fig. 4. For HVN, the NO concentration (mg NO/mg burned coal) obtained under the 21%O₂-79%CO₂ atmosphere was lower than that achieved under 21%O₂-79%N₂ conditions. In the 30%O₂-70%CO₂ and 35%O₂-65%CO₂ atmospheres, the NO concentration for HVN was slightly higher than that in the oxy-fuel atmosphere containing 21% of O₂, since higher oxygen concentrations increase the burnout value. However, the NO concentration in all the oxy-fuel atmospheres still remained lower than that in air. Therefore, only small differences in the reduction of NO in relation to the O₂

concentration in the three oxy-fuel combustion atmospheres were observed. Nevertheless, a slight tendency for the NO concentration to increase was detected as the O₂ increased. For coal BA, the differences in NO emissions between the different atmospheres studied were not as great, but a slight decrease in such emissions after oxy-fuel combustion was detected.

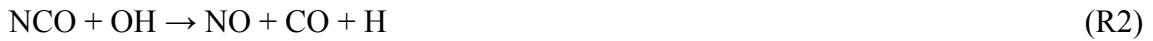
In order to facilitate a comparison of the behaviour of the coals under air and oxy-fuel atmospheres both with and without the addition of steam, NO concentrations (mg NO/mg burned coal) interpolated at a fuel ratio of 0.8 are shown in Fig. 5. It can be seen that the NO concentration of HVN in air and under oxy-fuel atmospheres decreased slightly after the addition of steam. There were however small differences between each of the three steam concentrations (Fig. 5a). For coal BA, the differences in NO concentration values for the different atmospheres were smaller (Fig. 5b).

Under air conditions, the thermal formation of NO resulting from the reaction between molecular N₂ and O₂ may occur at high temperatures (>1500°C). In this study, this route would make only an insignificant contribution to the formation of NO due to experimental temperature conditions. Under oxy-fuel conditions, the thermal formation of NO would be impossible due to the absence of N₂. Therefore, fuel-N would actually be the main source of NO emissions in the conditions established in these experiments.

Nitrogen in coal is converted to volatile nitrogen and char nitrogen during devolatilization. Thus, the fate of volatile-N and char-N becomes crucial for the formation of NO, and, hence, for determining the concentrations of NO in coal combustion systems. The volatile-N is transformed into either NO or N₂, while char-N reacts through a set of heterogeneous reactions as the char is oxidized.

On the other hand, two opposed mechanisms affect NO concentrations during coal combustion: firstly, the oxidation of fuel-N by oxygen and other oxidizing agents and, secondly, the reduction of the NO already produced by reducing agents.¹⁰ Consequently, the nitrogen product distribution will be largely dependent on the competition between the mechanisms of NO formation and destruction.¹³

As already mentioned, at the experimental temperatures used in this work, the predominant source of NO will be the nitrogen bound in the organic structures. A significant proportion of this coal-bound nitrogen will be released during the initial stages of combustion (devolatilization) as tars and as light gases such as HCN, NH₃ and HNCO.¹⁴ Evolved HCN is considered to be one of the most important volatile N-containing species formed during coal devolatilization at high temperatures because it is one of the main precursors of nitrogen oxides. In the presence of oxygen, the oxidation of HCN via NCO produces NO:



NH₃ may be formed by direct release from the solid matrix or from the hydrogenation of HCN on the char surface. Thus, by adding water vapour to the combustion reaction gas, Schäfer and Bonn¹⁵ found a parallel conversion route through the hydrolysis of HCN into NH₃ (temperature > 650 °C) (R3), followed by a subsequent oxidation reaction (R4):



However, the same authors also found that the parallel formation of NH₃ by hydrolysis (R3) not only led to the formation of NO (R4) at medium temperatures (650-800 °C),

but also to the decomposition of NO at elevated temperatures (800-1100 °C) (R5), according to the following reaction:



According to Normann et al.⁴, HCN and NH₃ react in a series of reactions and finally end up as NH and N, while subsequent reactions, which determine whether NO or N₂ is formed, are heavily dependent on the O/OH/H radical pool, which is related to flame conditions (stoichiometry, temperature and composition).³ The oxidation of HCN is controlled primarily by the HCN + OH reaction in case of increasing H₂O concentration. The oxidation of HCN starts at lower temperatures and the conversion of HCN to NO is inhibited by increase in H₂O concentration.¹⁶

In addition to volatile-N, varying amounts of coal N are retained in the char matrix and only released during the burning of the char. A full understanding of the reaction pathways for the conversion of char-N has not yet been achieved and is still an area of ongoing research.¹ Park et al.¹⁷ studied the chemistry of char-N release and its conversion to nitrogen-containing products after reacting with different reactant gases: O₂, CO₂ and H₂O. These authors found that, if char-N reacted with O₂, the major species formed were N₂ and NO. NO would be the primary product via the oxidation of the inherent nitrogen char surface species, C(N), (R6), whereas N₂ would result from the subsequent interaction of NO with the char surface (R8), as shown below:



Meanwhile, new nitrogen surface species, C(N), would be formed by the reaction of NO with the carbon char surface:



Finally, N₂ would be formed by reaction with the gas-phase NO:



Aihara et al.¹⁸ and Ashman et al.¹³ proposed the above reaction mechanism for the formation of N₂ during coal char oxidation. Glarborg et al.³ added that under kinetic control the reaction of char-N with O₂ (R6) is much faster than with NO (R8), whereas at high temperatures the reaction of char-N with O₂ becomes diffusion-limited, favouring the reaction of char-N with NO.

On the other hand, Park et al.¹⁷ found that the reaction of char-N with CO₂ mainly produced N₂ with a very high selectivity. During the reaction with CO₂ char-N may be released as NO at short contact times, but this NO would rapidly be reduced to N₂ by reaction with CO (R10), which would be produced from the reaction of the char-C with CO₂ (gasification reaction) (R9):



Park et al.¹⁷ also found that if the reactant gas was H₂O, the major species formed were HCN and NH₃, with lower concentrations of N₂. HCN would be the primary product from the reaction of char-N with H₂O, and the other products would result from reactions or interactions of the HCN with the char surface. Therefore, HCN may be released not only from coal devolatilization, but also from char-N when H₂O is added to the reactant gas, since the fate of the char surface nitrogen, C(N), will depend on the availability of hydrogen on the char surface. According to Park et al.¹⁷, hydrogen may come from H atoms on the char surface, C(H), or it may be provided by gas phase H₂, gas phase H atoms or steam:



The exact nature and structure of the C(H,N) species still requires further elucidation. The formation of HCN becomes greater at higher reaction temperatures, above 900 °C.¹⁹ The fate of the HCN formed from char-N will be determined later by the reactions R3-R5.

On the other hand, the NO may be reduced to form molecular nitrogen in an environment of low oxygen content in which the reduction of NO may occur. The reactants most likely to react with the NO in a reducing environment would be the hydrocarbon radicals formed from the released volatiles (reburning) or char-C. Andersson et al.⁵ pointed out that the char could play an important role as a catalyst for the destruction of NO, either directly, or by reaction with CO or H₂. The surface-catalysed reaction between NO and CO was illustrated above by R10.

Moreover, in the high-temperature regime, the reduction of NO on the char surface may be enhanced by an increase in the concentration of CO, since CO may contribute by removing oxides from the surface of the carbon as follows:²⁰



where C(O) represents a surface carbon oxide and C* a ‘free’ site, active in the reduction of NO. CO could result from the gasification reaction of coal char with CO₂ (R9), or alternatively the char may also interact with H₂O to form H₂ and additional CO (gasification reaction) (R14):

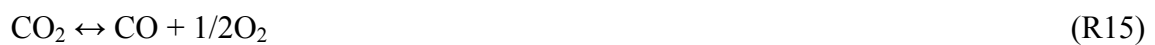


In this work, a significantly lower NO concentration was obtained under an oxy-fuel atmosphere with 21% of O₂ than under air conditions (Fig. 4). This was the case both in the steam and steamless atmospheres (Fig. 5), probably due to a higher NO reduction under oxy-fuel conditions as a result of the reaction of NO with CO (R10). Andersson et

al.⁵ found that the formation of NO from fuel-N in oxy-fuel combustion was the same as, or even slightly higher than, in air-firing conditions, whereas the destruction of NO was about 50% greater in oxy-combustion. It can be inferred therefore that the NO emissions during oxy-fuel combustion were lower than those of air-firing due to the increased destruction of NO formed under the O₂/CO₂ atmosphere. Okazaki and Ando⁸ also concluded that the reduction of NO to molecular N₂ due to chemical reactions in the combustion zone under oxy-fuel conditions was the main reason for the overall decrease (50-80%) in NO concentration. Liu et al.⁷ found that the higher CO concentrations inside the oxy-fuel combustion zone and within the vicinity of the combustion particles resulted in a further reduction of NO.

Moreover, Mendiara and Glarborg²¹ reported that an increase in the CO₂ concentration affected the concentrations of radicals (O/H/OH), and increased the probability of formation of N₂ from NH₃ (R5) instead of NO (R4). On the other hand, Giménez-López et al.²² concluded that high levels of CO₂ compete with O₂ for atomic hydrogen, through the CO₂ + H ↔ CO + OH reaction, thereby reducing the formation of chain carriers via O₂ + H ↔ O + OH, thus inhibiting HCN oxidation. These authors also observed a lower HCN combustion in the CO₂ atmosphere, accompanied by a higher level of CO formation and lower NO concentrations than under air combustion.

In our work, gasification of the char with CO₂ (R9) may have contributed to the increase in the production of CO during oxy-fuel combustion. Alternatively, in the flame zone under oxy-fuel conditions, CO₂ may dissociate into CO and O₂ via a strong endothermic reaction as follows:



However, as Toftegaard et al.¹ pointed out, there is a difference of opinion among researchers as to whether thermal dissociation (R15) or the gasification reaction (R9) is responsible for the significant increase in CO concentration in oxy-fuel combustion compared to air-firing.

Fig. 6 shows the CO concentrations (mg CO/mg burned coal) at the outlet under the different atmospheres studied (at a fuel ratio of 0.8) corresponding to the HVN and BA coals. It can be seen that the CO concentration was higher under the 21%O₂-79%CO₂ oxy-fuel atmosphere than under air conditions, surely due to the larger amount of CO produced from reactions R9 and/or R15. Hecht et al.²³ showed that CO may be formed by the char reacting with CO₂ in an oxy-combustion environment. If that was the case, the CO produced under oxy-fuel conditions would have reacted with NO (R10), since a lower NO concentration was found under the oxy-fuel atmosphere with 21% of O₂ than under air conditions. It is also possible that incomplete combustion occurred at the lower gas temperatures under oxy-fuel conditions (21%O₂-79%CO₂) leading to the production of additional CO. This would be explained by the high CO concentration observed under the 21%O₂-79%CO₂ atmosphere (Fig. 6).

In the presence of steam, the reactions R3 and R15 form additional CO. However, in general, no important differences were found in the CO concentrations after the addition of steam, either under the air or oxy-fuel combustion conditions for the HVN coal (Fig. 6a). The differences between the CO concentrations under the different atmospheres studied were also very small for the BA coal (Fig. 6b). In fact, the CO reacts with water according to the water gas shift reaction (R17), which probably happened to the CO formed in the atmospheres with steam:¹⁵



Although Figs. 4 and 5 show only small differences in the NO concentrations under the oxy-fuel atmospheres with increasing O₂ concentrations, the NO emissions seem to increase slightly with the O₂ concentration. The conversion of fuel-N to NO is expected to grow with the increase in O₂ in the feed gas due to the fact that a higher oxygen concentration in the feed gas causes a significant rise in temperature. Andersson et al.⁵ found that NO emissions per unit of fuel energy supplied fell under oxy-fuel combustion with 25% of O₂ compared to air-fired conditions. However, they found only small differences in the reduction of NO with the different O₂ concentrations in the feed gas (25, 27 and 29%) under oxy-fuel atmospheres.

As for the addition of water vapour, both under the air and oxy-fuel combustion atmospheres, a decrease in the NO concentration was observed for HVN when steam was added, even though no relevant differences were observed between different steam concentrations (Fig. 5a). In the case of the BA coal (Fig. 5b), the differences between the NO concentrations under the different atmospheres were very small.

The lower NO concentration after steam was added would be due to the formation of additional HCN in the presence of H₂O (R12) followed by the formation of NH₃ from HCN (R3), which in turn was due to the presence of H₂O, and subsequent destruction of NO at high temperatures (R5). In the presence of O₂, the HCN and NH₃ produced from H₂O could also have been transformed (R1, R2 and R4) to NO in the gas phase.⁵ However, Schäfer and Bonn¹⁵ observed that the rate of NO formation from HCN is delayed at temperatures above 710 °C. Likewise, these authors stated that the reaction of NO with NH₃, formed as an intermediate from HCN, could contribute to the release of N₂ (R5), since NH₃ may lead to an additional formation of NO at medium temperatures but to an additional decomposition of NO at elevated temperatures (800-1100 °C).

In our study, therefore, the NH_3 formed from HCN could have contributed to the reduction of NO concentration under the atmospheres with steam. Moreover, if char gasification with H_2O (R14) had occurred, H_2 had been formed, contributing to the reduction of NO concentration in atmospheres with steam. However, it is thought that this effect was only minor, since no relevant increase in burnout was observed after the addition of steam.

Cao et al.,²⁴ by means of computational fluid dynamics modelling, showed that a high concentration of nitrogen intermediates in the combustion zone –which can be achieved by wet recycling due to the presence of H_2O – favours the reduction of NO. Payne et al.²⁵ observed that the reduction of NO through reburning appeared to be greater in a wet recycle than in a dry one. Stadler et al.¹⁰ found lower NO_x emissions in wet oxy-fuel conditions than in dry oxy-fuel combustion after the numerical simulation of the NO behaviour. This is because less fuel-N is converted to NO in wet oxy-fuel conditions, as water vapour prevents the oxidation of intermediates from forming NO, and favours the reduction of NO from these intermediates. These authors also found that an increased oxygen concentration could undermine the positive effect that the increased water concentration would have on the NO emissions, as it is suggested in our study. The findings of our work also showed that the addition of CO_2 was more effective in reducing NO emissions than H_2O , in agreement with the results of Park et al.²⁶

4 CONCLUSIONS

NO emissions were lower during oxy-fuel combustion than in air-firing due to a higher reduction of NO by reaction with CO. A slight increasing trend in NO emissions was observed as the O_2 concentration increased in the oxy-fuel atmospheres. However, the

NO concentration fell when steam was added, both under the air and under the oxy-fuel atmospheres, but no relevant differences between the different steam concentrations were observed. This would be due to the lower formation of NO, since steam prevents the oxidation of intermediates from forming NO, and the higher reduction of NO by reaction with these intermediates, whose formation increases in the presence of steam.

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Figure captions

Fig. 1. Schematic diagram of the entrained flow reactor (EFR) used in the experiments.

Fig. 2. NO concentration of the HVN coal under different atmospheres at different fuel ratios.

Fig. 3. NO concentration of the BA coal under different atmospheres at different fuel ratios.

Fig. 4. Comparison of NO emissions of the HVN and BA coals under air and oxy-fuel combustion atmospheres at a fuel ratio of 0.8.

Fig. 5. Comparison of NO emissions of the HVN (a) and BA (b) coals under different atmospheres with and without steam at a fuel ratio of 0.8 (the $\text{H}_2\text{O}(\text{v})$ is added as a substitute for N_2 or CO_2).

Fig. 6. CO emissions of the HVN (a) and BA (b) coals under different atmospheres with and without steam at a fuel ratio of 0.8 (the $\text{H}_2\text{O}(\text{v})$ is added as a substitute for N_2 or CO_2).

Table 1. Proximate and ultimate analyses and high heating value of the coals

Sample	HVN	BA
Origin	Spain	Spain
Rank	sa	hvb
Proximate Analysis ^a		
Moisture content (wt.%)	1.12	1.20
Ash (wt.%, db)	10.64	6.91
V.M. (wt.%, db)	9.22	33.86
F.C. (wt.%, db) ^b	80.14	59.23
Ultimate Analysis (wt.%, daf) ^a		
C	91.68	88.44
H	3.49	5.48
N	1.91	1.93
S	1.58	1.12
O ^b	1.34	3.03
High heating value (MJ kg ⁻¹ , db)	31.78	33.08

sa: semi-anthracite; hvb: high-volatile bituminous coal.

db: dry basis; daf: dry and ash free bases.

^a The proximate analysis was conducted in a LECO TGA-601, and the ultimate analysis in a LECO CHNS-932.

^b Calculated by difference.

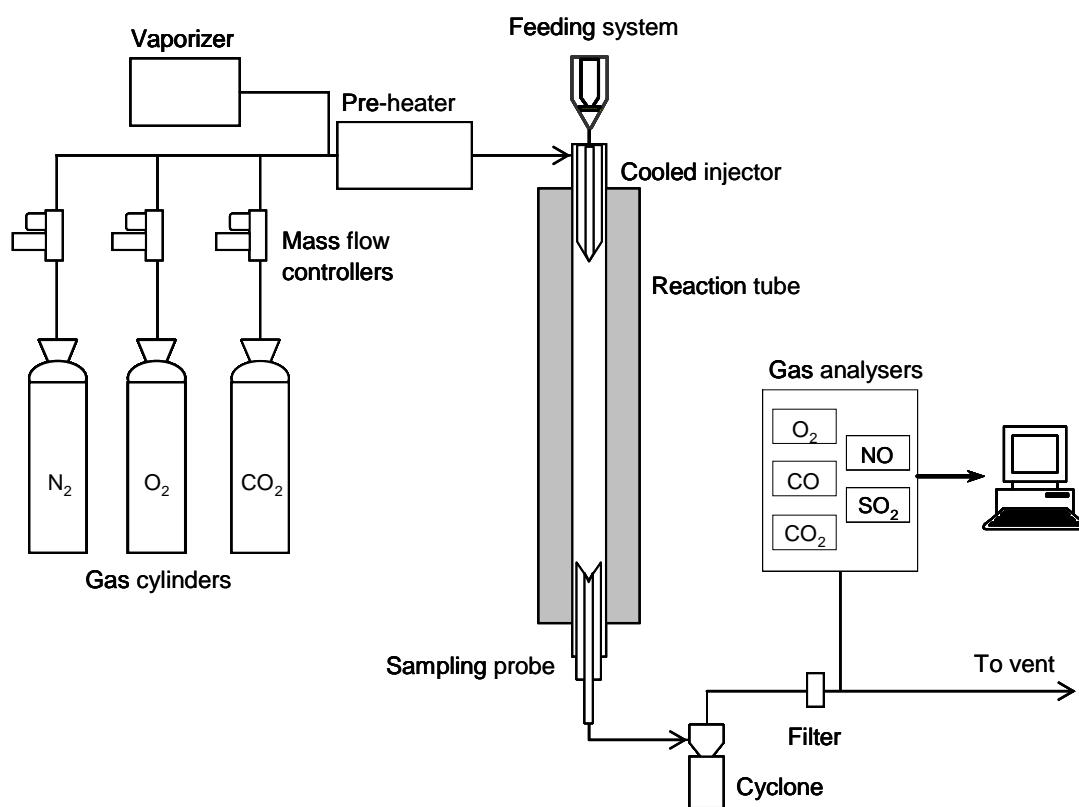


Fig. 1. Schematic diagram of the entrained flow reactor (EFR) used in the experiments.

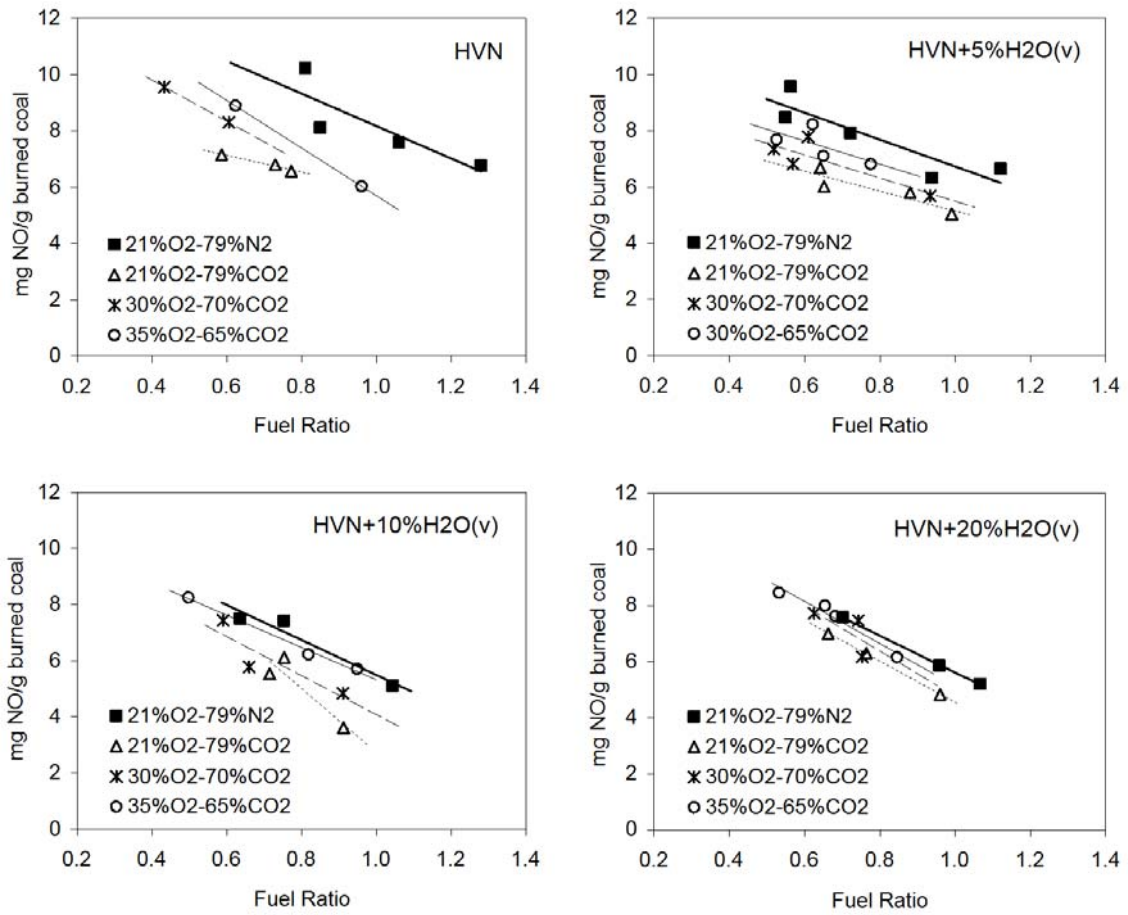


Fig. 2. NO concentration of the HVN coal under different atmospheres at different fuel ratios.

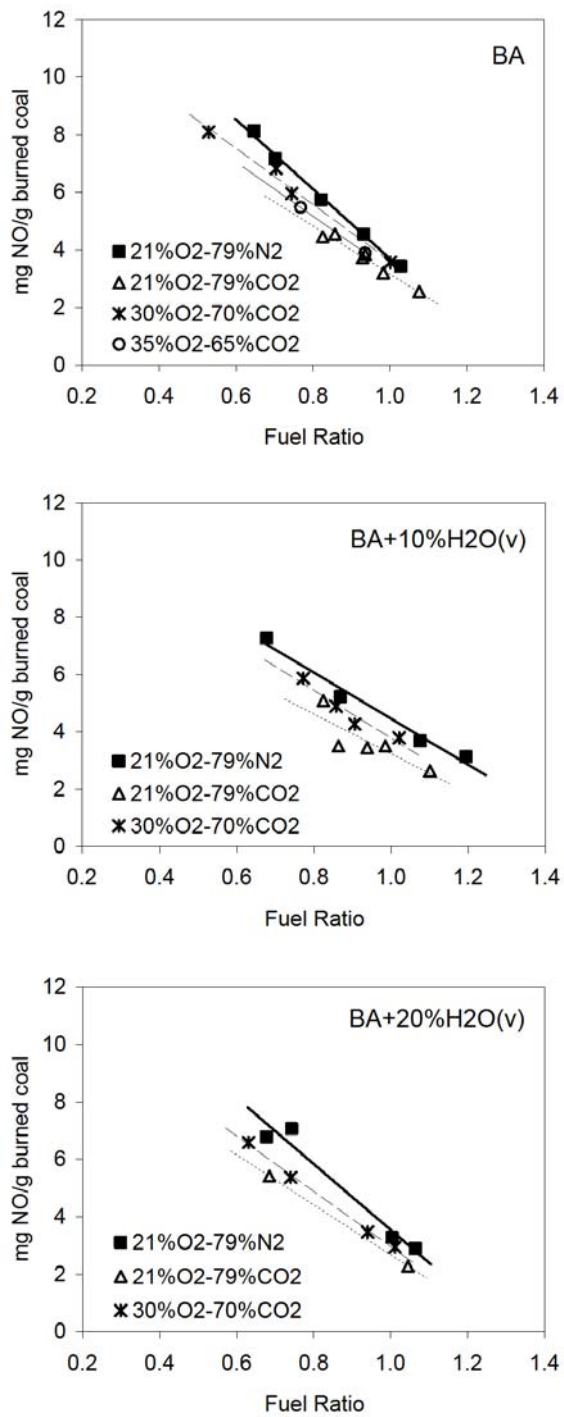


Fig. 3. NO concentration of the BA coal under different atmospheres at different fuel ratios.

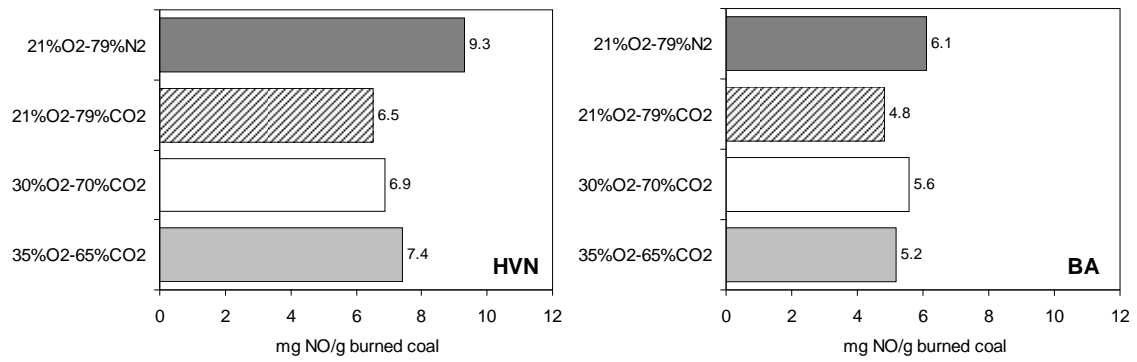


Fig. 4. Comparison of NO emissions of the HVN and BA coals under air and oxy-fuel combustion atmospheres at a fuel ratio of 0.8.

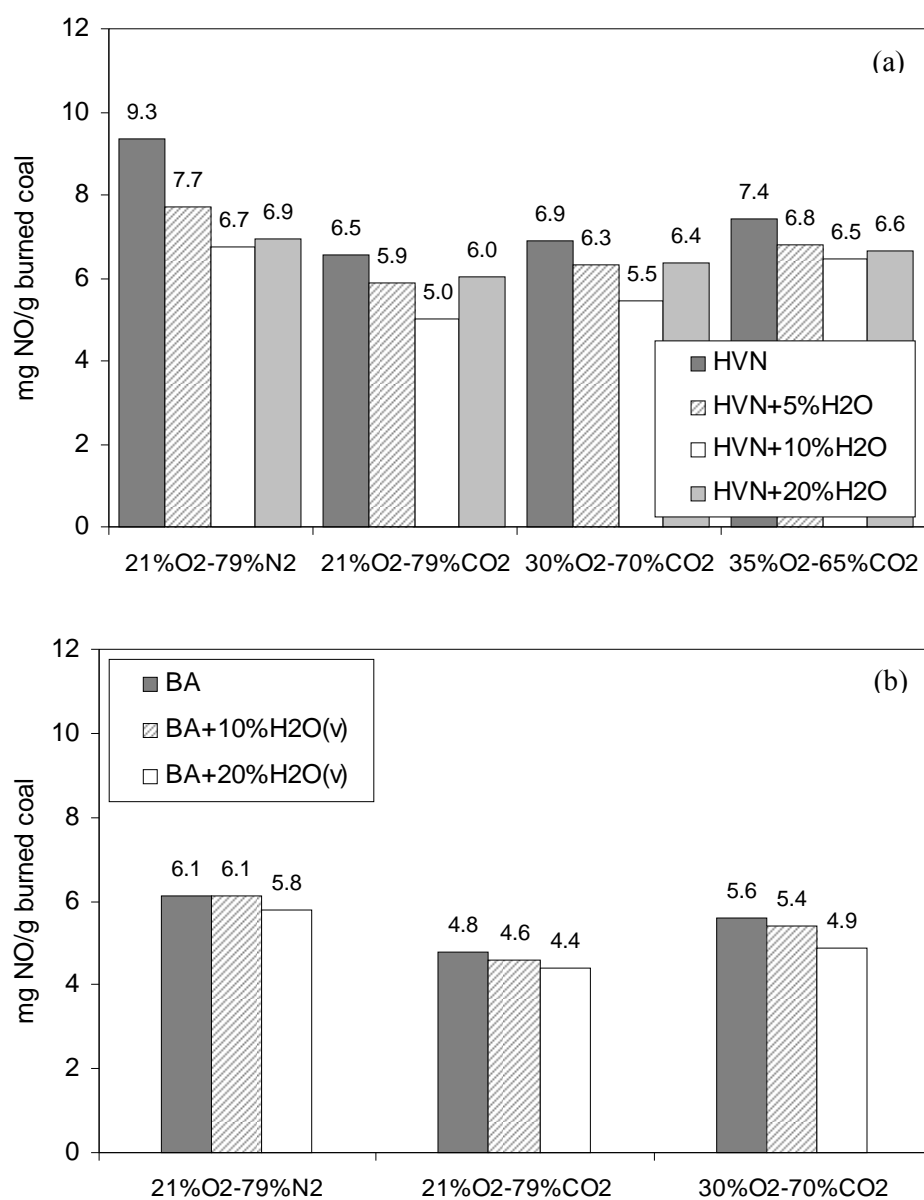


Fig. 5. Comparison of NO emissions of the HVN (a) and BA (b) coals under different atmospheres with and without steam at a fuel ratio of 0.8 (the H₂O(v) is added as a substitute for N₂ or CO₂).

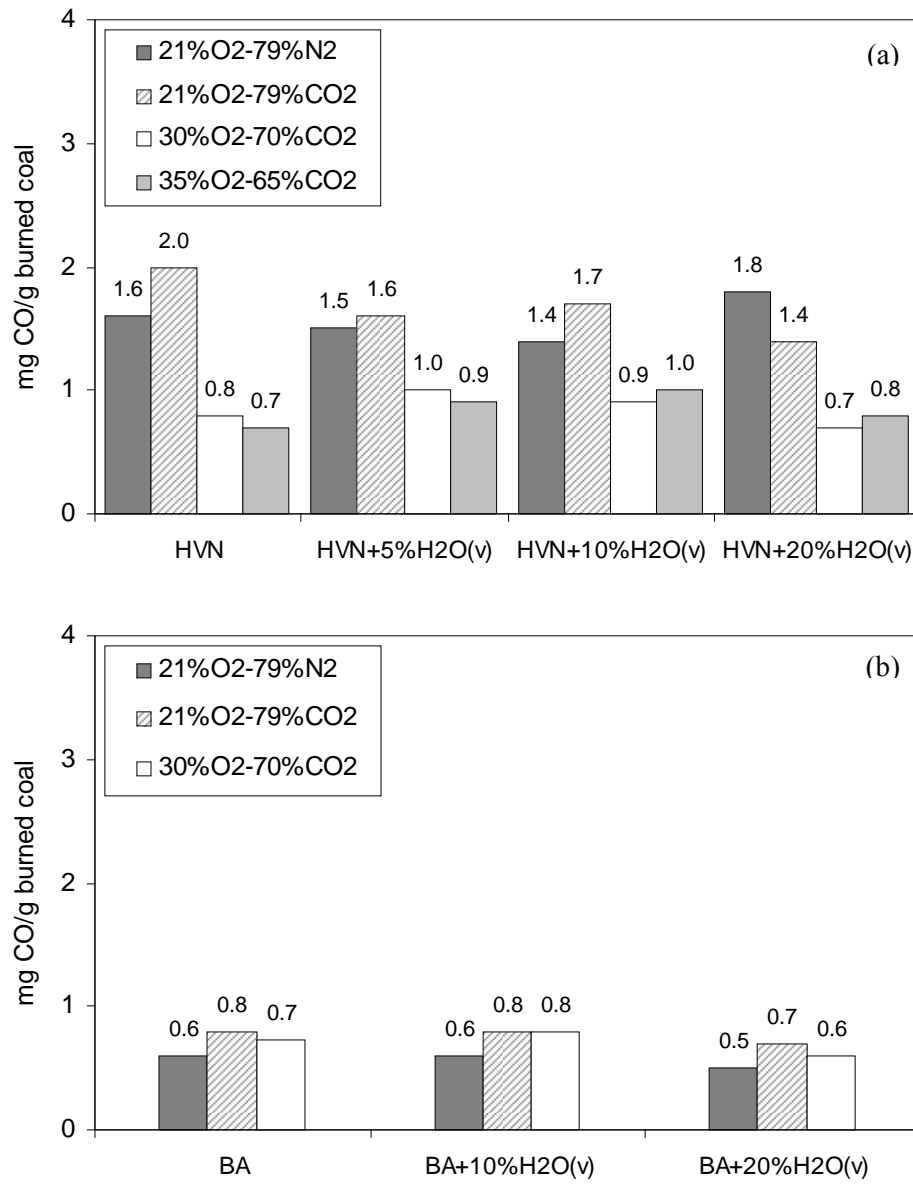


Fig. 6. CO emissions of the HVN (a) and BA (b) coals under different atmospheres with and without steam at a fuel ratio of 0.8 (the $H_2O(v)$ is added as a substitute for N_2 or CO_2).